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Estimation of free volume in polystyrene–polyphenylene ether blend probed by the positron annihilation lifetime technique

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Abstract

Variations of size, content and size distribution of free volumes in linear polystyrenes (PS) synthesized by radical processes, with the addition of miscible polyphenylene ether (PPE) in PS, were observed by positron annihilation lifetime measurements. The average free volume radius of polystyrene was proved to increase from 0.30 nm (PPE: 0%) to 0.34 nm (PPE: 100%) and the average intensity, relevant to free volume content, decreased with the increase of PPE. The size distributions of free volume of various PS to PPE ratios also reveal that average free volume size increases and that smaller free volumes decrease by the increase of PPE ratio. The evidence that the size distribution curve of PS and PPE mixture (1:1) is more similar to that of PS suggests that free volumes produced in PS are stable with the addition of PPE and that more positroniums annihilate in smaller free volumes generated in PS than in bigger ones formed by PPE, since numbers of free volume overwhelm those of PPE. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The industrial importance of polystyrene (PS) as mechanical and electrical materials urges the authors to study the behaviours of free volume parameters in PS and the correlation of the parameters to other molecular characteristics. Several of the properties of polymers can be well understood in terms of free volume present in an amorphous region of polymers in general. The authors synthesized several PS of different molecular structures—linear, three-armed and branched—by radical and anionic processes, characterized the microstructural state of these polymers, measured the free volume parameters by the positron annihilation lifetime technique and compared the temperature dependencies of free volume among these PSs [1,2]. The effect of the inclusion of low molecular weight impurities such as oligomers and plasticizer to free volume parameters was also studied [1–3].

Positrons, emitted from nuclei of sodium-22, annihilate in materials either by colliding with electrons to give the shortest lifetime component (τ_1: ~150 ps) and its intensity (I_1) or with electrons in the wall of free volumes and vacancies between crystalline and amorphous phases to give the intermediate τ_2 component (400–500 ps) and its intensity (I_2). Positron can form positronium (Ps), *para*-positronium (*p*-Ps) and *ortho*-positronium (*o*-Ps), with electron in an open space and annihilate. The *p*-Ps annihilates within 123 ps to contribute to τ_1 component. The *o*-Ps annihilates by pick-off reaction in ~ns contributing to the longest τ_3 component (0.8–3.5 ns) and its intensity (I_3). *Ortho*-Ps is utilized as an effective probe to estimate the free volume size and content since the lifetime (τ_3, in ~ns) and intensity of *o*-Ps are proved to be well correlated with the average free volume radius (R) and contents of free volumes, respectively [4].

$$\tau_3 = 0.5\left[1 - \frac{R}{R+0.166} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+0.166}\right)\right]^{-1} \tag{1}$$

The size distribution of the free volume is obtained by the application of an inverse Laplace transformation to the decay curve of positron annihilation [5,6].

In the present paper, the authors described the results obtained on the variation of size, content and size distribution of free volumes in polystyrenes, synthesized by radical processes, with the concentration of PPE. PPE is miscible in PS and introduced in PS to improve the plasticity and elasticity. Several studies have been reported on the effect of

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addition of miscible and immiscible foreign compounds to the size, content and size distribution of free volume by the blending [3,7,8] addition of plasticizer [9] to meet the important question as to which polymer–polymer system will be miscible from the molecular structure and what will be resulted to the molecular chain conformation.

2. Experimental

2.1. Specimens

Six mixtures of PS (specific gravity ρ:1.05, glass transition temperature T_g: 373 K, entanglement molecular weight: 18 700, characteristic ratio: 10.8) and PPE (ρ: 1.07, T_g: 478 K, entanglement molecular weight: 3620, characteristic ratio: 3.2) were synthesized and used without further purification unless otherwise mentioned. The specified physical and chemical properties of PS, a mixture of PS and PPE, and PPE are shown in Table 1. They were mixed, fused and moulded at an elevated temperature and then estimated as T_g from the composition between PS and PPE by 110 K and cooled down to a temperature 30–60 K lower than T_g. The prepared specimens were annealed in nitrogen atmosphere at temperatures 10–50 K higher than T_g in order to remove the distortion stored in the specimen during moulding.

2.2. Apparatus

A highly efficient fast–fast coincidence positron annihilation lifetime measuring equipment with time resolution of ~250 ps was used for the measurement. The details were described in the previous paper already published [10].

The positron source was 3.7×10^5 Bq ^{22}NaCl, deposited on a 10 μm-thick Kapton foil and folded. The source was sandwiched between two identical specimens (20 mm L × 20 mm W × 2 mm T). The positron annihilation curves were measured in 20 h to collect approximately 4×10^6 counts. The curves were fit by the PATFIT-88 computer program after the source correction of 15% and resolved into four components [11].

The size distributions of free volume were obtained by an application of the inverse Laplace transformation to annihilation decay curves using the CONTIN computer program [5,6].

3. Results and discussion

3.1. Variation of lifetimes and intensities of PS by the addition of PPE

A typical decay curve of positron annihilation of a mixture of PS and PPE is shown in Fig. 1(a). The annihilation decay curve is decomposed to four components. τ_3 component is divided to two sub-components, τ_{3a} and τ_{3b}. The τ_{3b} component is attributed to pick-off annihilation of *o*-positronium in free volumes. The origin of the τ_{3a} component has not interpreted yet among positron scientists, but the authors are confident that it is due to the annihilation of unlocalized Bloch-type *o*-positronium in the periodically arrayed small-size free volumes, as are seen in ice [12], polymer gel above volume phase transition temperature [13] or crystalline polyethylene [14] and polypropylene [15]. Variation of lifetime parameters (τ_1, τ_2, τ_{3a}, τ_{3b}) and intensities (I_1, I_2, I_{3a}, I_{3b}) against the compositional ratio of PS to PPE, obtained by the application of PATFIT-88 (POSITRONFIT and RESOLUTION) computer processing of decay curves, are shown in Table 2. The values of τ_1, τ_2 and τ_{3a} do not change by the increased addition of PPE. The longest lifetime, τ_{3b}, increases with the amounts of PPE. As to the relative intensities, I_1 and I_{3a} are almost constant, while the value of I_2 and I_{3b} decrease with increasing PS to PPE ratio.

3.2. Variation of average free volume sizes of PS on PPE composition

The dependence of an average free volume size of PS against the molar composition of PS and PPE is shown in Fig. 2. Because PS and PPE are miscible to each other, compositional dependence of free volume size of PS/PPE mixture is expected to follow the semi-additivity rule [3,9],

Table 1
Physical and chemical properties of PS, a mixture of PS and PPE, and PPE

Samples	1	2	3	4	5	6
PS wt%	100	70	60	50	25	0
PPE wt%	0	30	40	50	75	100
M_n	100 000			39 600		28 400
M_w	200 000					71 900
Specific gravity	1.05					1.07
Glass transition temperature (°C)	100			155		205
Entanglement molecular weight	18 700					3620
Characteristic ratio	10.8					3.2

PPE: poly (2,6-dimethyl-1,4-phenylene ether); PS: polystyrene.
Specimens were injection moulded after blending by extruder then annealed in N_2 at a temperature 10–15°C above T_g.

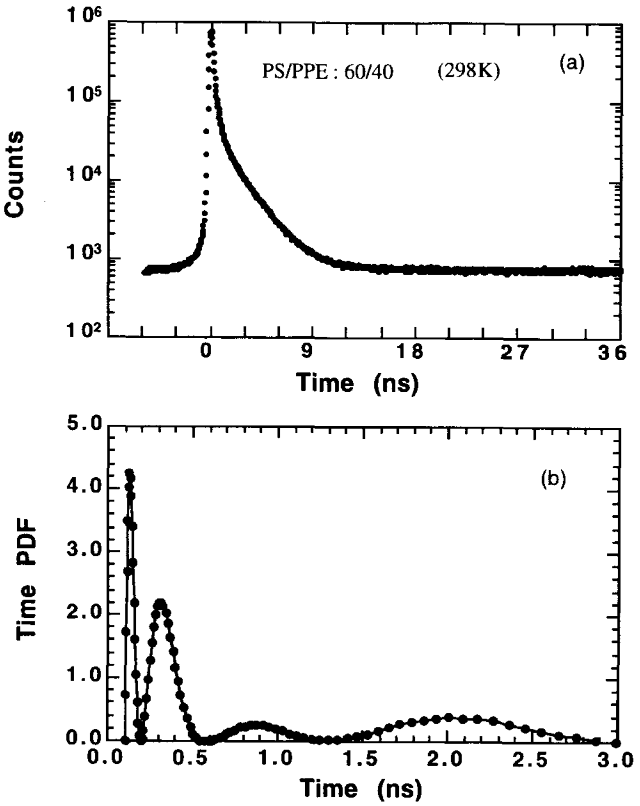

Fig. 1. Positron annihilation lifetime curve and distribution function of polystyrene (PS) and polyphenyl ether (PPE) at 298 K.

which is observed for PS–tetramethyl bisphenol–A polycarbonate (TMPC) and polyvinylchloride–dioctylphthalate plasticizer systems. As shown by the solid line in Fig. 2, average free volume sizes in the mixture of PS and PPE increases with the increase of PPE amounts. Bigger free volume size is observed in PPE than in PS. Yu et al. came to the conclusion that free volumes of PS are located near the crankshaft rotational spaces at the edge of backbone chains [16] from the evidence of the T_g shift to higher temperature with the increase of molecular weight of PS. We indicated that the free volume content in PS is inversely proportional to the logarithm of molecular weight at 333 K [2]. In other words, free volume content is proportional to the logarithm of numbers of polymer chain edges. Though the cause of the empirical evidence is not yet clarified, it strongly suggests that free volumes of PS generate close to chain ends since the shorter (longer) the polymer chain lengths, the more (less) the chain edges they have. The rigid crankshaft rotation of PS near the backbone chain ends may interfere the conglomeration of free volumes, and the average free volume size will not be varied, since the intrusion of PPE chains into the free volume at the ends of PS chains is difficult even at the thermal equilibrium in glassy state. The discussion is supported by the evidence that the free volume radius do not increase up to 1:1 mixture of PS and PPE. The formation of uniform free volumes is discussed again from free volume content in Section 3.3. On the contrary, less flexible, elastic and shorter chains of PPE are supposed to generate big free volumes in the course of backbone chain movements in between the chain ends and the free volume content become less even though PPE has far more numbers of chain ends than PS since more numbers of free volumes are required to generate a bigger free volume. The produced free volumes of PPE are speculated to have bigger and less uniform free spaces at thermal equilibrium below T_g, since harmonic movements among backbone chains of similar length are not in accord in half-frozen glassy state. The speculation is discussed again in Section 3.5 in connection with a size distribution of free volume.

The phenomenon of a concaved additivity of free volume size is considered to result by the less adaptability of PPE chains to the shape and size of free volume of PS according to the presence of phenyl groups in the backbone chains rather than the free volume deformation of PPE from spherical to ellipsoidal shape with the intrusion of PS [17–19].

3.3. Variation of average free volume contents with PS to PPE composition

The dependence of average free volume content on the ratio PPE/(PS + PPE) is shown by the dotted line in Fig. 2. The additivity rule is observed. The intensities of τ_{3b} component ($I_{PS/PPE}$) of the mixture are expressed as

$$I_{PS/PPE} = xI_{PS} + (1 - x)I_{PPE} \qquad (2)$$

where x is the ratio of PS to PPE.

If the conclusion proposed in Section 3.2, that free volumes of PS and PPE are generated near the of backbone

Table 2
Dependence of positron lifetime and relative intensity as a function of PPE/PS ratio

Compositional ratio of PS/PPE (wt%)	τ_1 (ps)	τ_2 (ps)	τ_{3a} (ps)	τ_{3b} (ps)	I_1 (%)	I_2 (%)	I_{3a} (%)	I_{3b} (%)
100/0	123 ± 5	343 ± 17	1055 ± 114	2119 ± 37	20.98 ± 1.5	31.63 ± 0.9	14.62 ± 1.2	32.77 ± 2.0
70/30	120 ± 6	313 ± 16	924 ± 78	2143 ± 26	19.85 ± 1.9	35.35 ± 1.1	14.98 ± 0.8	29.82 ± 1.1
60/40	119 ± 8	304 ± 13	659 ± 72	2211 ± 27	16.46 ± 2.0	37.62 ± 1.2	15.42 ± 0.7	30.49 ± 1.1
50/50	119 ± 6	306 ± 15	964 ± 67	2238 ± 27	20.78 ± 1.9	33.71 ± 1.2	16.36 ± 0.7	29.15 ± 1.0
25/75	121 ± 6	328 ± 12	1051 ± 78	2413 ± 34	19.45 ± 1.5	39.6 ± 0.9	14.63 ± 0.6	26.33 ± 1.1
0/100	120 ± 5	331 ± 10	1094 ± 65	2673 ± 36	19.18 ± 1.3	42.63 ± 0.8	15.04 ± 0.5	23.15 ± 0.8

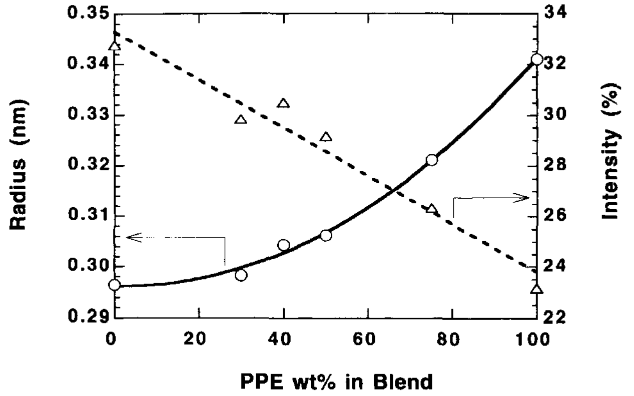

Fig. 2. Variation of average free volume size and contents as a function of PS and PPE composition.

chain ends of PS and in the middle of polymer chains in PPE, respectively, is valid and their free volumes function equally to the annihilation of o-Ps, the linear decrease of average free volume contents with the increase of rather linear PPE contents is the natural outcome of the linear decrease of the numbers of chain end of PS with the increase the PPE contents as long as the free volume of PS is prevalent in number. The evidence suggests that the interactions among polymer chains generated in mixtures of PS and PPE do not much affect the formation of free volumes. In other words, the exact additivity found for a free volume content suggests that the entanglement of chain ends of elastic PPE due to the rotation of the oxygen atom connected to the phenyl group into free volumes formed at the ends of PS is weak.

It is suggested that miscibility of PS and PPE in macroscopical scale does not necessarily mean that they mix with each other in subnano-scales. The conclusion is not modified until after the consideration using size distribution of the free volume in Section 3.5.

3.4. Variation of apparent free volume fraction with PS to PPE composition

The free volume fraction (f) in a polymer is defined as

$$f = 0.025 + \alpha_f(T - T_g) - \beta P \qquad (3)$$

where α_f is the formal delation coefficient at rubbery state and β is the compressibility of free volume at given temperature. It is generally difficult to know values of α and β for practical polymers, the authors define apparent free volume fraction (f_{app}) by the following equation

$$f_{app} = V_f I_{3b} \qquad (4)$$

where V_f is the free volume obtained applying τ_{3b} to Eq. (1). f_{app} works as a good parameter connected to free volume fraction since the absolute value of free volume fraction is not concerned, but the variation of total free volume fraction.

A variation of apparent free volume fraction for the PS–PPE system is shown in Fig. 3. It reveals that the multiplication of calculated free volume size and I_{3b} (numerical concentration), or apparent free volume fraction, is not varied much with the compositional ratio of PS to PPE up to 50% and increase gradually with the increase of PPE above 50%.

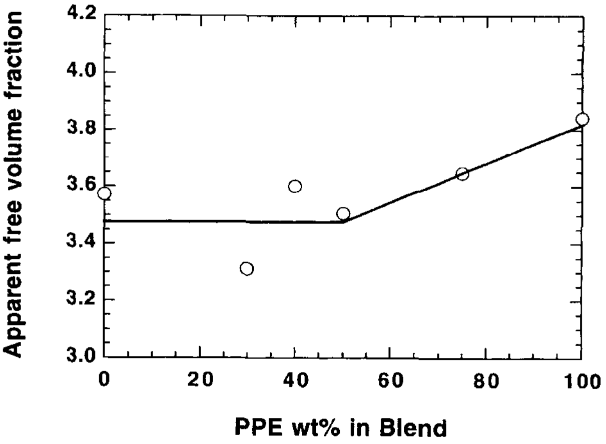

Fig. 3. Variation of apparent free volume fraction as a function of PS and PPE composition.

3.5. Variation of size distribution of free volume with PS to PPE composition

The size distributions are obtained by the application of an inverse Laplace transformation to positron annihilation decay curves of the PS/PPE system. The simulation of size distribution of free volume was carried so as to approximate the result to the average free volume size obtained by PATFIT-88.

Size distributions of free volume for PS, PS:PPE (= 1:1), and PPE are shown in Fig. 4, and dispersions of distribution curve are expressed in terms of full width at half maximum (FWHM) in Table 3. Narrower FWHM are observed for PS and 1:1 mixture of PS and PPE, and a dispersed distribution

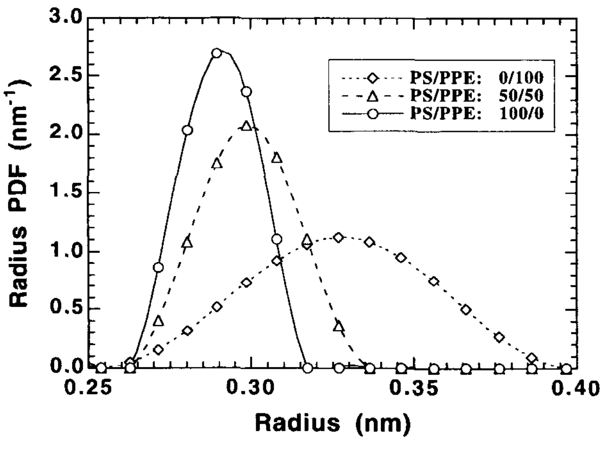

Fig. 4. Size distribution of free volumes of PS, mixture of PS and PPB, and PPE.

Table 3
Comparison of free volume parameters by PATFIT and CONTIN for PS, PS and PPE mixture and PPE

Compositional ratio of PS/PPE (wt%)	Free volume (*R*, nm)		FWHM (nm)
	FATFIT	CONTIN	
100/0	0.296 ± 0.006	0.291 ± 0.006	0.037 ± 0.005
50/50	0.306 ± 0.005	0.299 ± 0.007	0.048 ± 0.006
0/100	0.341 ± 0.004	0.328 ± 0.004	0.187 ± 0.007

is obtained for PPE. This evidence supports the speculation that the major location of free volumes due to rigid PS chains is at the backbone chain ends of PS, since the shape and size uniformity are easier to realize at the agglomerate free spaces of chain ends, and free volumes are suppressed to aggregates near chain ends even if elastic chain of PPE interact to the free volumes due to PS. The similarity in the size distribution of free volume for a 1:1 mixture of PS and PPE to that of PS suggests that the movement of most of the elastic chains of PPE is controlled so as not to disturb the chain ends of PS. It also indicates that the smaller free volume hole due to PS is neither influenced qualitatively nor deformed by the intrusion of methyl radical bound to the phenyl group of PPE.

Size distribution curves for PS and PPE mixtures are different from those simulated by the superposition of those due to PS and PPE and look more like that of PS. PPE has a bigger and wider distribution of free volume size, indicating the more elastic and less free the movements of its longer backbone chain. This result may be reflected in the higher T_g of PPE. The results of a polypropylene(PP)–ethylene/propylene/diene monomer (EPDM) blend shows similar characteristics obtained for PS–PPE [8]. Free volume size distribution of PP–EPDM blends are similar to PP by the addition of EPDM up to 30% and broadened for PP (60)–EPDM(40) blend. The phenomenon is interpreted as the simple dispersion of EPDM up to 30%, whereas the anomalous increase of size distribution is attributed to the generation of stress between PP and EPDM phase due to the non-uniform mixing or phase interaction. In the case of PS–PPE, similar effect can be if the PPE is mixed more than 60 mol%, as is shown not only in Fig. 2, but also Fig. 4.

3.6. Change of size and numerical concentration of free volume with temperature

The variation of free volume parameters—$\tau_{3b}(R)$, I_{3b} and apparent free volume fraction—observed for PS, 1:1 mixture of PS and PPE, and PPE in the temperature range from 25°C to 240°C is shown in Fig. 5(a–c), respectively. One of the most important physical characteristics related to the mechanical properties of polymers is T_g, below which temperature molecular mobility markedly decreases and viscosity and shear modulus increase. Our results on the temperature dependence of free volume radius, I_{3b} and apparent free volume fraction (Fig. 5), clearly show the transition temperatures. PS and PPE have different T_g glass transition temperatures, which increase with the increase of PPE contents. Crooked points designated in Fig. 5 for PS, 1:1 mixture of PS/PPE, and PPE are summarized in Table 4. Glass transition temperatures, determined

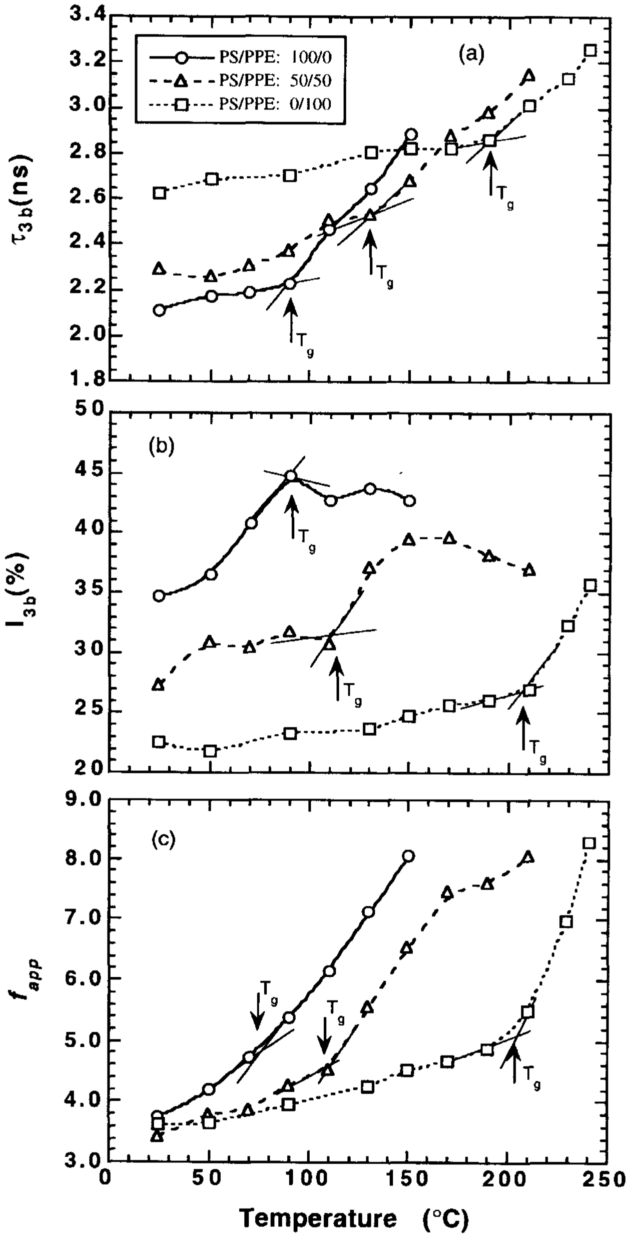

Fig. 5. Variation of average free-volume size (a), contents (b) and apparent free volume fraction (c) as a function of temperature.

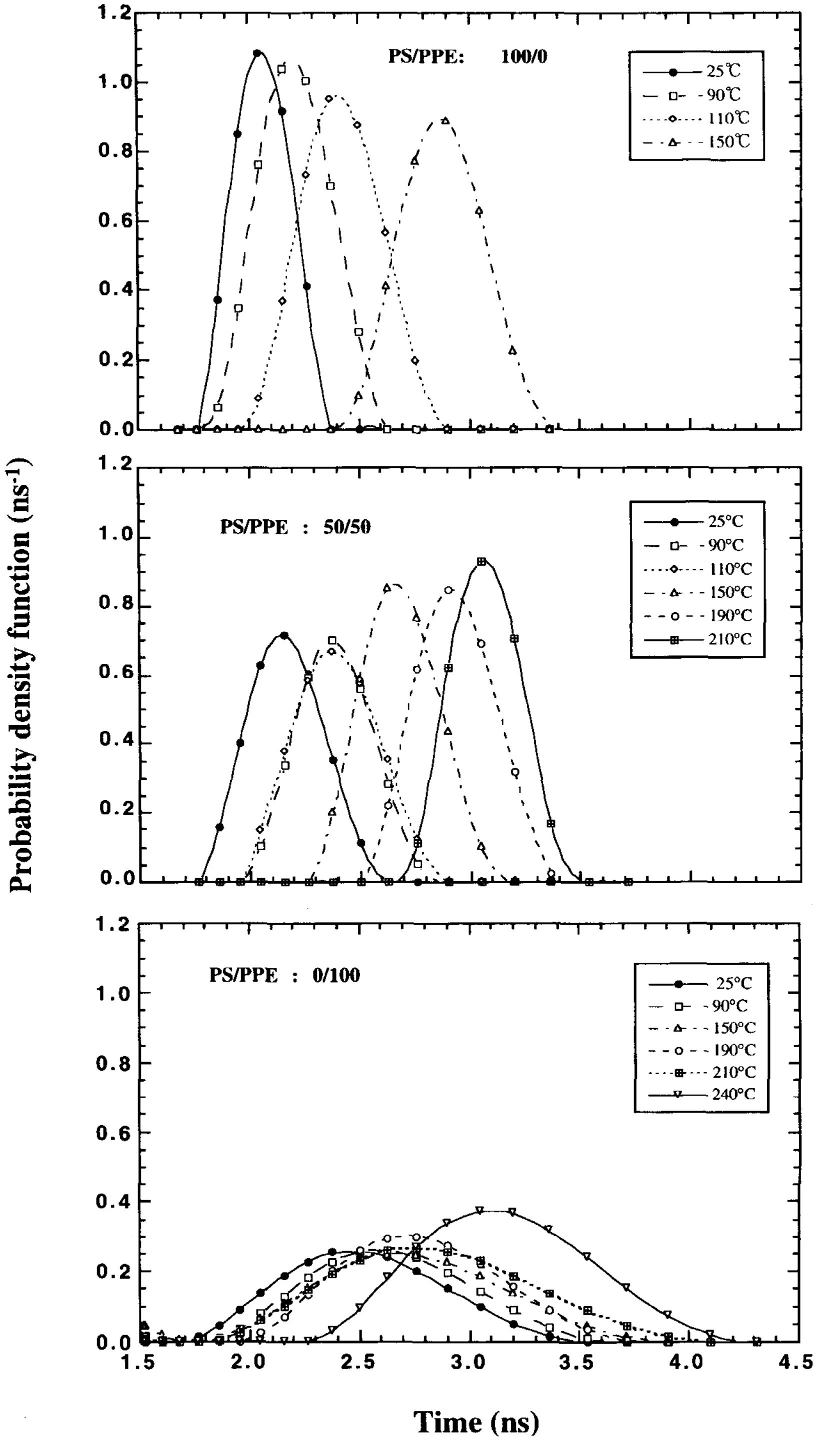

Fig. 6. Variation of size distribution of free volume of PS, mixture of PS and PPE, and PPE as a function of temperature.

by positron annihilation lifetimes, are found to always be lower than those observed by differential scanning calorimetry (DSC), as listed in Table 4. The origin of the smaller variations observed just below T_g are supposed to be due to an initiation of the liberation of a certain part of backbone chain. The glass transition temperature of the blend rises significantly with the increase of PPE since PPE has a considerably higher T_g relative to PS due to the more elastic backbone chain. Temperature dependence curves of I_{3b} and apparent free volume fraction also bend near T_g, decreasing gradient for PS, and increasing gradient for PS and PPE mixture and PPE in case of I_{3b} and increasing gradient for all samples in case of apparent free volume fraction. They suggest that free volume holes of PS aggregate and that new free volume holes are generated for PPE by the motion of backbone chains.

Table 4
Glass transition temperatures derived by the temperature dependence of free volume parameters

Parameters used	PS	PS/PPE (1:1)	PPE
DSC	100	155	205
τ_{3b}	90	130	190
I_{3b}	90	115	207
AFVF[a]	75	110	203

[a] Apparent free volume fraction.

The peak summits of size distribution of free volume for PS, PS and PPE (1:1) and PPE shift to the bigger side, keeping the profile of the distribution or FWHM by the elevation of temperature.

4. Conclusions

The average free volume radius of PS is proved to increase and numerical concentration of free volume content decrease linearly with the increase of PPE contents. The distinct variation is observed for the size distribution of free volumes, average free volume size increasing and smaller free volume fraction decreasing by the increase of PPE content. This evidence suggests that bigger free volumes are generated near the backbone chain of PPE as the amount of PS decreases and *o*-Ps are favoured to form and annihilate in bigger free volumes. Temperature dependence of free volume size shows T_gs of PS and PPE (1:1) mixtures shifts to higher temperature with the increase of PPE to PS ratio.

Free volume study reveals that PS and PPE blend are miscible in macroscopical scale, but they do not mix with each other in sub-nanoscopical scale.

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